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Volume, Enthalpy and Entropy of Activation of the Diels-Alder Reaction of Dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate with 1-Hexene

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Abstract: *Pressure and temperature effects on the reaction rate of dimethyl1,2,4,5-tetrazine-3,6-dicarboxylate with 1-hexene were investigated. The activation volume (-26.7 cm^3 mol^{-1}, 298.1 K) is in agreement with the conservation of all four nitrogen atoms in transition state. Densitometry, ^1H NMR and calorimetric studies of the reaction indicate nitrogen molecule loss by the intermediate just after its formation. Partial molar volumes in acetone of diene (127.2), 1-hexene (127.6) and the resulting adduct (206.9 cm^3 mol^{-1}) were determined.*

INTRODUCTION

For the common Diels-Alder reaction there are many known examples confirming the "Alder rule".[1] Dewar[2] predicted the possibility of realization of the inverse electronic demands that was confirmed from the rate measurements of the Diels-Alder reaction with dimethyl-1,2,4,5-tetrazine-3,6-dicarboxylate.[3,4] This diene exhibits enhanced activity in reactions with nonactivated alkenes and especially with cycloalkenes. As was shown[5], the reaction rate can be predicted more precisely taking into account orbital interactions,the energy balance of breaking and making bonds and the distance between the C_1 and C_4 reacting atoms of 1,3-diene. The more exothermic are reactions, the greater is the stabilization of the activation barrier and in the reaction rate enhancement.[5-7] This fact can be clearly seen from the comparison of cyclopentadiene and 9,10-dimethylanthracene activity in the Diels-Alder reaction with cyanoethylenes.[8] For the reaction in dioxane of tetracyanoethylene (electron affinity, EA=2.88 eV, ΔH_{r-n} = -88 kJ mol^{-1}) 9,10-dimethylanthracene (IP=7.04 eV) is 30 times more active than cyclopentadiene (IP=8.57 eV, ΔH= -113 kJ mol^{-1}) , but for the reaction with a weak acceptor like acrylonitrile (EA =0.02 eV) it is cyclopentadiene that is 12 times more active.

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